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16. ABSTRACT

The purpose of Work Assignment 19, 36, 56 under Contract 68-02-4442 was to support Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency in its effort to monitor the hazardous composition, if any, of fly ash from various types of incinerators using different types of combustible materials. The analytical determination of dioxins in environmental samples in the parts per billion, trillion, and quadrillion levels requires meticulous, time-consuming, and very complex sample preparation and analysis procedures.

A major part of this task was devoted to the evaluation of various extraction techniques of fly ash and cleanup of sample extracts by column chromatography. Several chromatographic media and eluting solvents were investigated. Each step in the sample preparation was evaluated by using ^{14}C-radiolabeled 2,3,7,8-tetrachlorodibenzo-p-dioxin and octochlorodibenzo-p-dioxin as a tracer. Radiolabeled dioxin allows the analyst to stop and evaluate each step of the procedure, each extract, and each column eluate fraction by liquid scintillation computing. To validate the radiometric assay, dioxin was confirmed by gas chromatography/mass spectrometry.

This report contains recovery data of spiked 2,3,7,8-tetrachlorodibenzo-p-dioxin and octochlorodibenzo-p-dioxin in carbon-free fly ash and fly ash containing from 0.1% to 10% carbon.

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2,3,7,8-Tetrachlorodibenzo-p-dioxin Fly Ash Octobhlorodibenzo-p-dioxin OCDD-^{14}C TCDD-^{14}C Extraction Column Cleanup Particulate		

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EFFICIENCY OF DIOXIN RECOVERY FROM FLY ASH SAMPLES DURING EXTRACTION AND CLEANUP PROCESS

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an indepth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

PCDDs and PCDFs are being evaluated for future emissions regulations because of their toxicities. Acceptable measurement methodology is critical for proper assessment of the impact on the environment of these emissions from stationary sources. Development and validation of measurement methods are key components for producing an acceptable method. This study was undertaken to perform as part of the development and validation work on a method for the quantification of PCDDs and PCDFs emissions from stationary sources.

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ABSTRACT

The purpose of Work Assignments 19, 36, and 56 under Contract 68-02-4442 was to support Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency in its effort to monitor the hazardous composition, if any, of fly ash from various types of incinerators using different types of combustible materials.

The data from investigations of the efficiency of dioxin recovery from fly ash samples during sample extraction and subsequent column cleanup of sample extracts are discussed in this report. Steps of the extraction and the column cleanup procedures were evaluated by using radiolabeled ^{14}C-dioxins as tracers. Sample extracts and eluate fractions were analyzed by liquid scintillation counting (LSC) and the results confirmed by gas chromatography/mass spectrometry (GC/MS). Recovery data of spiked 2,3,7,8-tetrachlorodibenzo-p-dioxin-^{14}C (TCDD-^{14}C) and octachlorodibenzo-p-dioxin-^{14}C (OCDD-^{14}C) in carbon-free fly ash and fly ash containing from 0.1 to 10% carbon are discussed. The data indicate that the amount of carbon in the fly ash may affect the efficiency of dioxin recovery. The data from this study will be used to determine procedural areas that need improvements or modifications to allow the accurate determination of trace levels of dioxins and furans in fly ash. Various extraction techniques of fly ash and cleanup of sample extracts by column chromatography were evaluated.

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SECTION 1

INTRODUCTION

Numerous types of waste are generated daily on a large scale by U. S. producers and consumers. Among these waste types are household trash, agricultural residues, municipal wastes, and industrial wastes. The astronomical volume of waste and its potential health hazard will not allow haphazard disposal such as uncontrolled discarding of waste into the environment. Although many of the components of waste can readily biodegrade, methods of disposal such as open burning, discarding in surface water, or placing into landfills are no longer desirable. Thus, waste management has become concerned with treatment technologies and new methods that will minimize the toxicity and volume of waste generated. The enactment of environmental laws, regulations, and guidelines has helped the authorities in their attempts to monitor and control the waste that is discharged into our environment.

The Resource Conservation and Recovery Act (RCRA) of 1976 obligates the U. S. Environmental Protection Agency (EPA) to develop regulations and standards to manage the handling of hazardous waste from its initial generation to its final disposal. The individual states will be responsible for the implementation of these standards and regulations. The Comprehensive Environmental Response Compensation and Liability Act (CERCLA or "Superfund") of 1980 is concerned with abandoned hazardous waste sites and authorizes the EPA to provide for emergency response and cleanup of chemical spills and for the prevention of the release of hazardous substances into the environment.

Current efforts are directed at finding economic, effective, and efficient alternatives to land burial. Hazardous waste incineration and municipal incineration of waste, coupled with energy recovery, are practices that are gaining favor and promise to increase in the near future (1). Properly designed and operated hazardous waste incineration systems can attain the 99.99% destruction and removal efficiency required by law (2).

The incineration of municipal wastes, however, generates a fly ash that is composed of 75 to 95% inorganic matter in addition to a complex mixture of organic compounds, elemental carbon, and water (3). Approximately 100 organic compounds have been identified by Eiceman et al. (4), using GC/MS, in fly ash samples collected from municipal incinerators in Japan, Canada, and the Netherlands. Included in this list are polycyclic aromatic hydrocarbons, polychlorinated phenols, polychlorinated benzenes, polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzo-p-dioxins (PCDDs). The estimated concentrations of total organic mass extracted ranged from 1 to 30 $\mu g/g$, and the sum of PCDD isomers was an estimated 2 to 10 ng/g. Although the distribution of trace organic compounds was quite different in the samples studied from the different countries, PCDDs and PCDFs were present in every sample, suggesting that these compounds are formed universally during incineration processes even though the combustible materials and the incineration conditions may vary (4,5).

In other studies, chlorinated compounds have been shown to be adsorbed on fly ash produced from the incineration of municipal waste and some studies have shown that fly ash may play a catalytic role in the chlorination of

organic species (6-8). PCDDs and PCDFs have been detected in fly ash from the incineration of polychlorinated biphenyls (PCBs) (9), chlorobenzenes (10), and municipal refuse (11). Also, PCDDs have been shown to result from the exposure of coal to hydrochloric acid and chlorine (Cl_2) at 600 °C (12). Some of the isomers of PCDDs are suspected to be highly toxic, mutagenic, and teratogenic. With more large-scale incinerators being built in urban areas, the release of airborne particulates and the fly ash that is generated may have a serious impact on the environment and could cause adverse health effects. Thus, simple, routine, and reliable sampling and analytical methods are needed for determining hazardous compounds in fly ash, particularly trace levels of the PCDDs.

Existing methods for the analytical determination of ppb and ppt concentrations of PCDDs/PCDFs in environmental samples are very difficult and time consuming. The cleanup may require many steps and the quantitative determination must be performed with great care.

Currently, several different analytical procedures are being used for the extraction, cleanup, and analysis of PCDDs and PCDFs. Albro and Parker (13) and Smith and co-workers (14) have published extensive cleanup procedures for PCDDs and PCDFs in environmental samples. RCRA Method 8280 and ASME's draft method entitled "Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF)," prepared by Group C--Environmental Standards Workshop sponsored by the American Society of Mechanical Engineers, U. S. Department of Energy and U. S. Environmental Protection Agency, September 18, 1984, have been applied to fly ash samples for the determination of PCDDs and PCDFs. Using these procedures, significantly different levels of PCDDs and PCDFs have been found in similar fly ash samples. These differences may be due to changes in combustion parameters or inherent errors in the analysis methods such as nonreproducible extraction and cleanup procedures. Many investigators have noted differences in the apparent recovery efficiencies of different extraction procedures.

Kooke et al. (15) reported that extraction efficiencies of PCDDs and PCDFs from fly ash varied widely and were dependent on the method of extraction. In one study, relative extraction efficiencies for seven different methods ranged from 1 to 100% on a single fly ash sample. Their work demonstrated that Soxhlet extraction with benzene or toluene gave the best results and that the highest dioxin yield was consistently found on acid treatment of fly ash prior to extraction. Those methods that involved simple shaking or ultrasonic treatment of fly ash with an extracting solvent gave poor recovery. Although their study compared methods with respect to the highest extraction efficiency, it did not allow measurement of the absolute efficiency of the methods.

A second study on fly ash from a Canadian municipal incinerator showed that concentrations of different PCDD congener groups varied with fly ash particle size (16). Tetra- and penta-CDDs were more prevalent on the larger particles (550 mm), and octa-CDD was more prevalent on the smaller particles (30 mm).

Eiceman et al. (3) extracted fly ash using an ultrasonic extraction technique but they did not determine accuracy and absolute recovery efficiencies. An advantage of this technique may be seen with fly ash samples that contain very fine particulates that may obstruct the solvent flow through the extraction thimble in Soxhlet extraction or may pass through into the refluxing flask.

Karasek and Viau (6) analyzed fly ash from a high-temperature rotary kiln municipal waste incinerator and found PCDDs as well as chlorinated benzenes, chlorinated cyclohexanes, and chlorinated biphenyls. Among the 82 individual compounds they found were hydrocarbons, alkyl phthalates, alkyl benzenes, alkyl cyclohexanes, alkyl phenols, and PAHs. The fly ash samples were extracted with benzene using an ultrasonication technique.

Steiglitz et al. (17) compared a number of different pretreatment and extraction procedures with regard to recovery of PCDD/PCDF from fly ash. Direct Soxhlet extraction, extraction with an ultrasonic probe, and refluxing with an acidic solvent mixture were the techniques evaluated. The highest dioxin yield was obtained using an acid digestion with excess dilute HCl, followed by freeze-drying of the residue and hot extraction with toluene. Like Kooke, they showed that higher recovery was obtained when an acid digestion step was included in the procedure. This improvement in extraction may be due to an opening of the pore structure of the fly ash.

The sorptivity of different fly ash samples for organic compounds in general has been shown to vary greatly. Studies with ^{14}C-labeled PAHs as radiotracers demonstrated that the extraction recoveries of PAHs from fly ash are inversely proportional to the number of rings in the PAH molecule and that aromatic compounds are more strongly adsorbed than aliphatic hydrocarbons (18). No correlations were observed between sorptivity and surface area, density particle size, moisture, percentage of hydrogen, oxygen, sulfur, and moisture, or noncombustible residue. However, total carbon content was shown to parallel sorptivity. These results indicate that analyses of some fly ash samples for certain organic compounds may be seriously biased if not corrected for extraction recoveries or sorptivity losses. PCDD and PCDF analyses may also be expected to show sorptive losses. These losses may become more pronounced as the concentration levels of PCDDs/PCDFs decrease, the number of chlorines added to the ring structures increases, or the nature of the fly ash changes.

Because of the topics discussed above, particularly the prevalence of PCDDs in fly ash samples from municipal waste incinerators, the suspected toxicity of several of the dioxin isomers, and the apparent variability in recovery efficiency with different procedures or different samples, there is an urgent need to study the factors that affect the recovery of PCDDs from fly ash samples. Current procedures, both for extracting PCDDs from fly ash and for cleanup of sample extracts, need to be evaluated. Once the critical parameters affecting these processes are identified, a protocol can be developed to assure accurate measurement of PCDDs. Thus, a sound data base can be gathered to accurately assess the PCDD emissions produced during the incineration of hazardous and municipal wastes. These data can then be used to evaluate the environmental health risks resulting from this method of waste management.

The subsequent sections of this report describe the efforts of Southern Research Institute (SRI) to evaluate various extraction techniques to remove dioxins from fly ash and to clean-up sample extracts by column chromatography. General chromatographic media and eluting solvents were investigated. Each step in the sample preparation was evaluated by using ^{14}C-radiolabeled 2,3,7,8-tetrachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin as tracers. Radiolabeled dioxins allowed the analyst to stop and evaluate each step of the procedure, each extract, and each column eluate fraction by liquid scintillation counting. To validate the radioassay, dioxin was confirmed by gas chromatography/mass spectrometry. This study was conducted by SRI under Work Assignments 19, 36, and 56 of Contract 68-02-4442, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

SECTION 2

CONCLUSION

- The carbon content of fly ash and the nature of the carbon may affect the extraction efficiency of dioxin. As the carbon content of fly ash increased, the efficiency of spiked TCDD-^{14}C and OCDD-^{14}C recovery decreased.

- Toluene is a better extracting solvent for dioxin than methylene chloride in the Soxhlet extraction procedures. This difference was more discernible as the carbon content of the fly ash increased and when the dioxins of higher molecular weights were extracted.

- The recommended time for Soxhlet extraction is 24 hours. Extraction for longer time periods did not significantly improve the efficiency of dioxin recovery from the fly ash samples.

- The volume and composition of eluting solvents used for column cleanup of sample extracts are critical and must be monitored to prevent unexpected losses of dioxins. After the Soxhlet extraction procedures, the toluene extracting solvent should be exchanged with a higher boiling aliphatic hydrocarbon. Thus, when the concentrated extract is applied to the head of the acid/base-modified silica gel column, the dioxin will be in an aliphatic solvent that is less polar.

- If trace compounds in complex environmental samples are to be accurately determined, appropriate analytical procedure must be selected and carefully followed by the analyst. The extraction and cleanup procedures used in the analyses of fly ash for the determination of PCDD and PCDF must be validated by the laboratory and the individual analyst performing the analysis. Laboratory control samples (spiked matrix samples) must be carried through the entire analytical method, which includes sample preparations, cleanup of sample extracts, and instrumental analysis. Procedural details and analytical techniques, such as the cycling of solvent in the Soxhlet extractor, transfer of the solutions, the exchange of solvents, the packing of the chromatographic media into columns, and the volume and composition of the extracting solvents, are extremely important. Variable loss of dioxins can occur in each of these steps. All extracts, eluate fractions, and residues generated during an analysis need to be saved for additional analysis when the recovery of spiked standards or surrogate standards are extremely low in the initial analysis. If there is a question about low recovery after the final eluate is analyzed, the other eluates may have to be analyzed. With every set of samples that are analyzed, laboratory control samples, surrogate spiking standards, replicate analyses, and method blanks must be included. The extraction and cleanup procedures to determine dioxins in fly ash samples must be implemented by or under close supervision of analysts with experience in trace analyses.

SECTION 3

RECOMMENDATIONS

The recommendations for future investigations are as follows:

- Continue to evaluate Soxhlet extraction and column cleanup procedures for other polychlorinated dioxins and furans using radiolabeled ^{14}C-tracers. The recovery efficiency may vary with increased chlorination of the dioxins and furans.

- Evaluate proposed extraction and cleanup protocols on other types of fly ash samples. The change in combustion parameters and the type of combustible materials will determine the final chemical composition of the fly ash. Thus, the characterization of the fly ash will affect the recovery efficiency of each major class of organic compounds.

- Evaluate and validate the proposed protocol for lower concentrations of PCDDs (ppt) using ^{14}C-dioxins as tracers.

- Investigate high-performance liquid chromatography (HPLC) as an alternative cleanup option to classical adsorbent cleanup procedures.

- Develop a final protocol incorporating the most acceptable sample preparation steps. Evaluate the protocol with field samples from combustion sources and their associated process residues.

- Using radiolabeled ^{14}C-tracers, evaluate the efficiency of dioxin and furan recovery from a sampling train used to collect combustion effluents.

SECTION 4

TECHNICAL APPROACH

GENERAL CONSIDERATIONS

To establish base line data on the efficiency of dioxin recovery from fly ash samples, the ASME's draft method entitled "Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF)" was selected for initial evaluation. Fly ash samples that were spiked with tetra-CDD were analyzed by the ASME's draft method as written and without significant deviations. As experimental data were generated, potential problem areas in the ASME's method were noted. Discrete changes were incorporated in the ASME's method and the modified procedures were reevaluated with fly ash samples spiked with tetra- and octa-CDD. Thus, the data presented in this report represent an evolution from the original ASME's method to the final modifications of the ASME's method proposed by SRI.

FLY ASH SAMPLES

A single source of fly ash that was generated from a medium-sulfur bituminous coal, was used in this study. The fly ash was collected from the ESP hoppers at The Gaston Steam Plant, Alabama Power Company in Wilsonville, Alabama. The chemical composition of the fly ash, determined by SRI, is shown in Table 1. The carbon content of the fly ash was 5%. A carbon-free fly ash was prepared by heating the native fly ash for 16 hours in a muffle furnace set at 750 °C. In later studies, this carbon-free fly ash was spiked with known amounts of various types of carbon.

TCDD-^{14}C AND OCDD-^{14}C STANDARDS

Fly ash samples were spiked with either 2,3,7,8-tetrachlorodibenzo-p-dioxin-Ring-UL-^{14}C (TCDD-^{14}C) or octachlorodibenzo-p-dioxin-Ring-UL-^{14}C (OCDD-^{14}C) obtained from Pathfinder Laboratories, Inc (Sigma Chemical Co.). TCDD-^{14}C as received from the supplier was 33.2 mCi/mMol in a total volume of 475 μL of tetrahydrofuran. The entire content was diluted to 1 mL with tetrahydrofuran. With a 10-μL syringe, 5 μL of TCDD-^{14}C was transferred to a 500-mL volumetric flask containing approximately 250 mL of methylene chloride. The mixture was manually shaken and diluted to 500 mL with an additional amount of methylene chloride. OCDD-^{14}C was supplied as a solid and was 20.6 mCi/mMol. The entire content was dissolved in 5 mL of methylene chloride. With a 50-μL syringe, 41 μL of OCDD-^{14}C was diluted to 500 mL with methylene chloride. These solutions became standard spiking solutions of TCDD-^{14}C and OCDD-^{14}C. Their specific activities were monitored throughout the study.

CHEMICALS AND REAGENTS

Solvents

High purity, distilled-in-glass hexane, methylene chloride, toluene, ethyl acetate, benzene, and cyclohexane (Burdick and Jackson Laboratories, Inc.) and

TABLE 1. CHEMICAL COMPOSITION OF THE NATIVE FLY ASH USED IN DIOXIN STUDY

Oxide	Weight percent[a]
Li_2O	0.08
Na_2O	0.46
K_2O	2.5
MgO	1.2
CaO	2.8
Fe_2O_3	14.2
Al_2O_3	27.3
SiO_2	47.9
TiO_2	1.9
P_2O_5	0.83
SO_3	0.63
Carbon[b]	5.0

[a]Analysis was performed on ignited sample and reported as weight percent of oxides.

[b]Carbon was determined on the native fly ash.

anhydrous n-nonane (Gold Label, Aldrich Chemical Company, Inc.) were used in this study.

Carbon

Some fly ash samples were spiked with carbon which came from three sources:

- Carbon black from Arthur H. Thomas Company,
- Activated carbon, AX-21 grade, Super A, from Anderson Development Company, and
- Pittsburgh-activated carbon from Calgon Corporation.

The Calgon carbon was ground and sifted through a wire sieve, 180 mesh. The other carbons were were supplied as a fine powder and were used without additional preparation. Spiking levels of carbon in the fly ash samples did not exceed 10% (wt/wt).

Chromatography Media

Three types of chromatography media were used in the column cleanup procedures:

- Basic alumina, AG10, 100-200 mesh from Bio-Rad,
- Silica gel, Bio-Sil A, 100-200 mesh from Bio-Rad, and
- Activated carbon, AX-21 grade, from Anderson Development Company combined with Celite 545 from Fisher Scientific Company.

EXTRACTION METHODS

Soxhlet Extraction

A Soxhlet extraction apparatus with a coarse, glass-fritted extraction thimble containing approximately 1 g of anhydrous sodium sulfate was used. Fly ash samples (10 g) in the extraction thimbles were spiked with 5 mL of TCDD-^{14}C spiking solution (88.5 ng; 9,145 pCi) or OCDD-^{14}C spiking solution (230 ng; 10,304 pCi). The spiked samples were allowed to air dry overnight prior to extraction. In the initial phase of this study, several solvents and time periods were evaluated for the efficiency of dioxin recovery. Extraction times were either 24 or 48 hours, and the extracting solvents were 150 mL of methylene chloride or toluene. Also, some samples were extracted sequentially with methylene chloride followed by toluene. At the end of the extraction period, all extracts were concentrated to 1 mL on a hot plate with a stream of dry nitrogen. A few samples that gave poor recovery of OCDD-^{14}C when extracted with toluene were treated with hydrochloric acid solution and re-extracted for 24 hours with toluene.

Tissumizer-Agitation Extraction

Fly ash sample (10 g) was placed in a 250-mL round-bottom, glass centrifuge bottle and spiked with 5-mL of TCDD-^{14}C spiking solution (88.5 ng; 9,145

pCi). The spiked samples were allowed to dry prior to extraction. Several extracting solvents and periods of agitation were investigated. The extracting solvent (150 mL of methylene chloride or toluene) was added to the sample, which was then agitated for 5 or 10 min with a Tekmar Tissumizer Probe. The sample was centrifuged for 15 min at 2000 rpm. The extracting solvent was decanted into a 300-mL beaker. An additional 50 mL of solvent was added to the extracted fly ash and the sample was manually shaken for 2 min and centrifuged again. This second extract was pooled with the initial portion of extract and the pooled extracts were concentrated to 1 mL on a hot plate with a stream of dry nitrogen. Some of the samples that were initially extracted with methylene chloride were re-extracted with toluene.

COLUMN CHROMATOGRAPHY CLEANUP METHODS

Chromatography Media

Basic alumina--The alumina was activated by heating at 600 °C in a muffle furnace for 16 h and allowing to cool to room temperature in a desiccator. An alumina column was prepared by adding 3 g of basic alumina to a 13-cm O.D. glass column fitted with a glass frit and stopcock.

Silica gel--Silica gel was activated by heating at 130 °C for 6 hours. Acid-modified silica gel was prepared by combining in a screw-capped bottle 100 g of Bio-Sil A with 44 g of concentrated sulfuric acid and agitating to mix thoroughly. Aggregates were dispersed with a stirring rod until a uniform mixture was obtained. Base-modified silica gel was prepared by combining in a screw-capped bottle 100 g of Bio-Sil A and 39 g of a 1 M sodium hydroxide solution and agitating to mix thoroughly.

AX-21 Carbon/Celite 545--In a glass bottle fitted with a Teflon-lined cap, 10.7 g of AX-21 carbon and 124 g of Celite 545 were combined and agitated to mix thoroughly.

Column Chromatography Cleanup

The columns described below and shown in Figure 1 were used to clean up the extracts of the fly ash samples. The selection of these columns and solvents were based on the recommendations of the ASME's analytical procedures to assay stack effluent samples for PCDDs and PCDFs. All eluate fractions were either saved or solvent exchanged with toluene or n-nonane and submitted for liquid scintillation counting (LSC) and, in some cases, were analyzed by gas chromatography/mass spectrometry. The eluates that were applied to the head of the basic alumina columns or the carbon/celite columns were concentrated to 1 mL of hexane prior to separation on the columns.

Combination silica gel column--A glass column fitted with a Teflon stopcock and a small plug of glass wool at the bottom of the column was filled with, in sequence, 1 g of silica gel, 2 g of based-modified silica gel, 1 g of silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. The column was prewashed with 30 mL of hexane. The sample extract (from the Soxhlet extraction step) was diluted with 5 mL of hexane and applied to the top of the column. The vial that contained the extract was rinsed with two 5-mL portions of hexane which were applied to the column. The column was eluted with 90 mL of hexane. The eluates comprised of the sample solvent plus the two 5-mL

LIQUID CHROMATOGRAPHIC CLEANUP COLUMNS

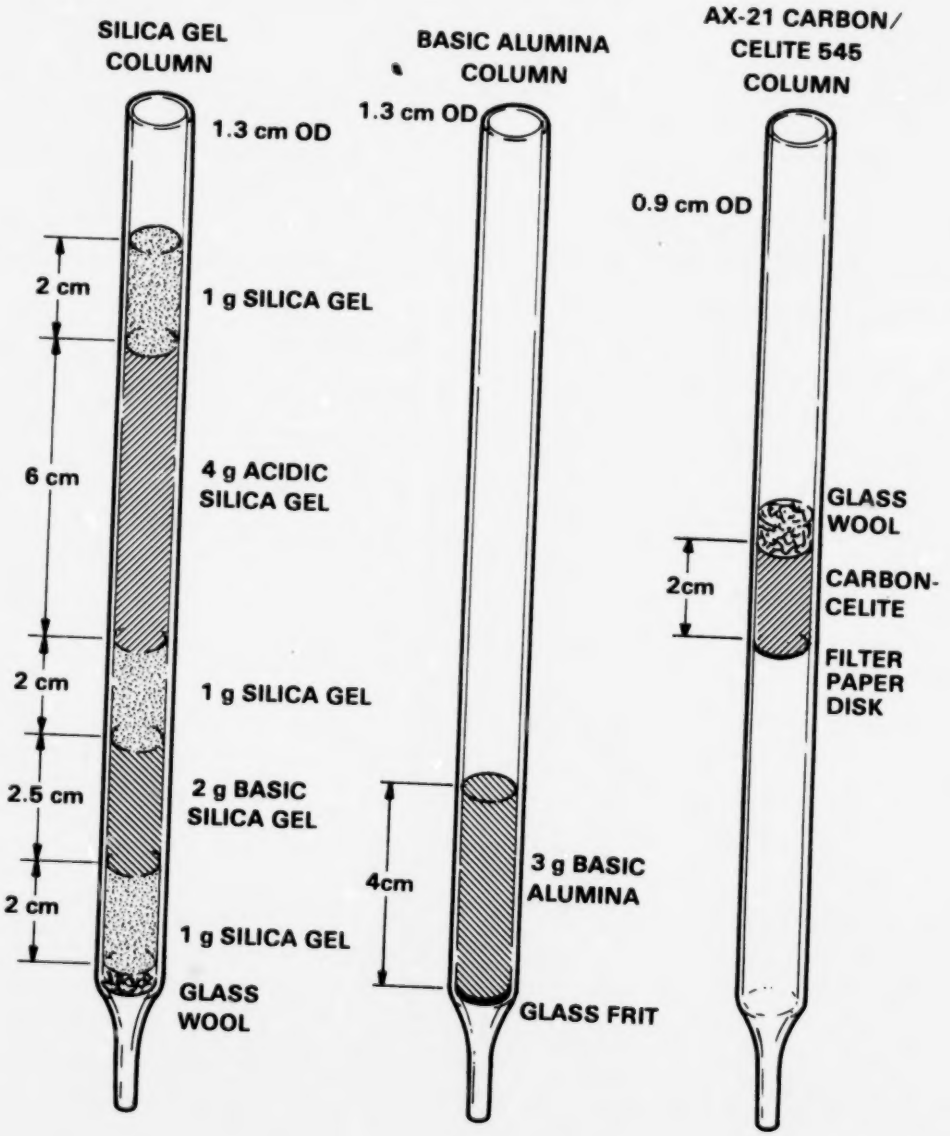

Figure 1. Liquid chromatographic cleanup columns.

rinses were collected separately from the 90-mL elution. The eluates were concentrated to 1 mL as described elsewhere.

Basic alumina column--A glass column fitted with a Teflon stopcock and a fritted glass filter was filled with 3 g of basic alumina. The column was prewashed with 5 mL of hexane. The 1-mL concentrated eluate from the combination silica column was applied to the top of the basic alumina column. The vial that contained the extract was rinsed with three 5-mL portions of hexane which were applied to the column. The column was eluted sequentially with 10 mL of 8% methylene chloride in hexane and 15 mL of 50% methylene chloride in hexane. Each of the eluate fractions was concentrated to 1 mL.

AX-21 Carbon/Celite 545 column--A glass tube (6-mm I.D.) was fitted with a filter paper disk (Whatman No. 54) approximately 3 cm from the top and was filled with the AX-21 Carbon/Celite 545 mixture to form a 2-cm length of the carbon/celite. Then a glass wool plug was inserted. The column was prewashed in sequence with 2 mL of 50% benzene in ethyl acetate, 1 mL of 50% methylene chloride in cyclohexane, and 2 mL of hexane. The 1-mL concentrated eluate from the alumina column was applied to the top of the column. The vial that contained the extract was rinsed with 1 mL of hexane which was applied to the column. The column was then washed first with 2 mL of 50% methylene chloride in hexane and then with 2 mL of 50% benzene in ethyl acetate. The column was inverted and eluted with 4 mL of toluene. The final eluate was analyzed either by LSC or GC/MS.

LIQUID SCINTILLATION COUNTING (LSC)

For LSC, extracts or eluates were concentrated to 1 mL in 20-mL scintillation vials using a nitrogen blowdown technique. The sides of the scintillation vials were washed down several times with n-nonane during the reduction of solvent volume and a solvent exchange was made with n-nonane. Then 20 mL of scintillator (RPI Complete Counting Cocktail 3a20) was added to each scintillation vial and analysis was performed by LSC.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

The TCDD-^{14}C used in this study consisted primarily of native 2,3,7,8-TCDD with only a small fraction being radiolabeled. Therefore, the GC/MS analysis was conducted by monitoring ions at mass-to-charge ratio indicative of the native compound. As an internal standard, $^{13}C_{12}$-2,3,7,8-TCDD was added to the sample extract.

The selected-ion-monitoring GC/MS conditions for 2,3,7,8-TCDD are listed below:

Instrument:	VG Analytical Model 70S Magnetic-sector mass spectrometer and data system with a Hewlett-Packard Model 5890A gas chromatograph

Column:	HP-5 (Crosslinked 5% phenyl methyl silicone) fused-silica capillary column, 25-m x 0.32-mm I.D. x 0.17 mm film thickness (Hewlett-Packard Co, Avondale, PA)
Carrier gas:	Helium, 2 mL/min
Injection mode:	1 to 2 μL splitless with a 45-s purge delay
Inj. port temp.:	275 °C
Oven temp. prog.:	130 °C for 3 min, to 300 °C at 15 °C/min
MS parameters:	Direct capillary interface to the ion source. Selected ions for TCDD m/z 320, 322, 324, 332, 334 for 50 ms each. Source temperature set to 200 °C.

SECTION 5

RESULTS AND DISCUSSION

Existing methods for the analytical determination of PCDDs/PCDFs in environmental samples in parts per billion and parts per trillion concentrations are very difficult and time consuming. Because environmental samples are complex in composition, one or more column cleanup procedures of the sample extracts are often required. As stated in Section 1, some investigators have noted differences in the levels of dioxin found in similar types of fly ash. These differences may be caused by any combination of factors such as the overall composition of the combustible materials, the operational conditions of the incinerators, the inherent errors in the analytical method, the limitation of the specific extraction procedures applied to the fly ash, or the selection of the column cleanup procedures applied to the sample extracts. Although extraction and cleanup procedures have been closely studied, in most cases the absolute recovery efficiencies were not reported, especially those associated with each step of the overall analytical method.

In this study, radiolabeled TCDD-^{14}C and OCDD-^{14}C with liquid scintillation counting (LSC) were used to trace the PCDDs through each of the steps associated with an analytical method based on ASME's analysis of stack effluents from combustion processes. The quantification of TCDD-^{14}C and OCDD-^{14}C by LSC allow for lower detection limits than does quantification by GC/MS. Also, the use of radiolabeled PCDD is more time and cost effective because separation from impurities (those not radiolabeled) is relatively unimportant, especially in preliminary screening or evaluation of analytical procedures.

TCDD-^{14}C AND OCDD-^{14}C STANDARDS

To keep the variables to a minimum, throughout the entire study we used one standard solution of TCDD-^{14}C in methylene chloride (17.71 ng/mL and 1828 mCi/mL) and another one of OCDD-^{14}C in methylene chloride (46.0 ng/mL and 2061 mCi/mL). Also, all fly ash samples were spiked with 5 mL of a standard solution of radiolabeled dioxin to give either 8.85 ng of TCDD-^{14}C per gram of sample (8.85 ppb) or 23.0 ng of OCDD-^{14}C per gram of sample (23.0 ppb). With each set of analyses, duplicate standards were submitted for LSC. Each 5 mL of standard solution of radiolabeled dioxin was concentrated to 1 mL, as were the various Soxhlet extracts and column cleanup eluates. In the initial stages of our investigations, we concentrated all fractions or extracts without a solvent exchange. Although the counting efficiency varied with the composition of the concentrated solvent, the total specific activity did not vary (Table 2). For consistency, all subsequent submittals for LSC were in 1 mL of n-nonane.

Linear-regression analysis of the calibration data for TCDD-^{14}C in Table 3 gave a slope of 1043.5 pCi g ng^{-1} with an intercept of -11.279 pCi and a correlation coefficient of 0.99998. The response in pCi was linear between 1.77 ng/g and 17.7 ng/g of TCDD-^{14}C per sample. Linear-regression analysis of the calibration data for OCDD-^{14}C gave a slope of 435.98 pCi g ng^{-1} with an intercept of 171.01 pCi and a correlation coefficient of 0.99981. The response in pCi was linear between 4.61 ng/g and 46.1 ng/g of OCDD-^{14}C per sample.

TABLE 2. SPECIFIC ACTIVITY AND COUNTING EFFICIENCY OF TCDD-^{14}C AND OCDD-^{14}C STANDARDS

Standard	5 mL Standard concentrated to:	Averaged Specific activity, pCi	Averaged Counting efficiency, %
TCDD-^{14}C	1 mL CH_2Cl_2	9205 ± 46	62 ± 0.8 (n = 4)
	1 mL Toluene	9105 ± 89	83 ± 0.8 (n = 6)
OCDD-^{14}C	1 mL Toluene	10297 ± 169	85 ± 1.8 (n = 16)
	1 mL n-Nonane	10315 ± 68	86 ± 0.9 (n = 12)

n = number of replicates.

TABLE 3. SPECIFIC ACTIVITY CALIBRATION DATA FOR TCDD-^{14}C AND OCDD-^{14}C

Standard	Standard/ sample, ng/g	Specific activity, pCi
TCDD-^{14}C	1.77	1847
	3.54	3707
	5.31	5475
	5.31	5556
	7.08	7385
	8.85	9173
	8.85	9249
	14.2	14799
	17.7	18474
	17.7	18461
OCDD-^{14}C	4.61	2067
	4.61	2096
	9.22	4076
	13.8	6198
	13.8	6164
	18.4	8359
	23.0	10345
	23.0	10415
	36.9	16252
	46.1	20080
	46.1	20265

EXTRACTION METHODS

Although we were mainly interested in monitoring the recovery efficiencies of dioxin from fly ash samples using a Soxhlet extraction procedure, we also investigated a procedure in which fly ash and an extracting solvent were briefly but vigorously agitated using a high-speed tissumizer. In the initial stages of the Soxhlet extraction procedure fly ash samples were extracted for 24 hours with methylene chloride followed by an additional 24-hour re-extraction with toluene. In later studies single extractions with only toluene were included. A general outline of these procedures is given in Table 4.

Soxhlet Extraction

Three types of fly ash samples were used in this investigation: native fly ash, zero-carbon fly ash, and carbon-spiked fly ash. Elemental analysis of the native fly ash indicated the presence of approximately 5% carbon (wt/wt). Both the native fly ash and the zero-carbon fly ash were spiked with various amounts of carbon. Thus, fly ash samples containing from 0% to 10% carbon (wt/wt) were extracted for 24 hours with methylene chloride followed by an additional 24 hours with toluene or were extracted with only one of the two solvents for 24 hours. The recovery efficiencies for TCDD-^{14}C from fly ash spiked at 8.85 ppb are given in Table 5 and for OCDD-^{14}C from fly ash spiked at 23.0 ppb are given in Table 6. These results indicate that the carbon content of the fly ash and the nature of the carbon may affect the extraction efficiencies of PCDDs if methylene chloride is used as the extracting solvent in the Soxhlet extraction procedure. Also, the data demonstrate that the recovery of OCDD-^{14}C with toluene was less than that of TCDD-^{14}C. Extraction times >24 hours with either solvents did not significantly improve the recovery efficiencies of TCDD-^{14}C or OCDD-^{14}C. In one study in which the recovery of OCDD-^{14}C was <50% when the native fly ash was spiked with 5% AX-21 carbon, the extracted samples were treated with acid and re-extracted with toluene. An additional 35-65% of OCDD-^{14}C was recovered from the fly ash. These results confirm the data reported by Kooke (15) and Stieglitz (17).

A general summary of one set of results is given in Table 7. This table represents some of the major variables we investigated--methylene chloride and toluene as extracting solvents, TCDD-^{14}C and OCDD-^{14}C as spiked radiolabeled standards. three levels of carbon content of fly ash samples, and a single 24-h extraction using a Soxhlet extractor. If the carbon content of the fly ash is zero, then recovery of PCDDs is not a problem. At 5% carbon content, toluene is the preferred solvent for extracting PCDPs from the fly ash that we used in this study. However, depending on the total carbon content of the fly ash and the different sources of the carbon, other extraction procedures may be more desirable.

Tissumizer-Agitation Extraction

In the initial phase of this study, we briefly investigated a quick and simple method to evaluate its potential for determining the level of TCDD-^{14}C in fly ash samples. A general outline of the technique is given in Table 4, Section B. This procedure can reduce the extended extraction times and the

TABLE 4. GENERAL OUTLINE OF INITIAL EXTRACTION PROCEDURES

A. Soxhlet Extraction

1. Weigh 10-g fly ash sample
2. Spike with 5 mL PCDD-^{14}C standard
3. Allow fly ash to dry
4. Extract for 24 h with 150 mL methylene chloride
5. Concentrate extract to 1 mL
6. Re-extract sample for 24 h with 150 mL toluene
7. Concentrate extract to 1 mL
8. Submit both extracts for liquid scintillation counting

B. Tissumizer-Agitation Extraction

1. Weigh 10-g fly ash sample
2. Spike with 5 mL PCDD-^{14}C standard
3. Allow fly ash to dry
4. Agitate for 5 min in 150 mL methylene chloride
5. Centrifuge for 15 min at 2000 rpm
6. Remove extract
7. Shake manually fly ash for 2 min in 50 mL methylene chloride
8. Centrifuge for 15 min at 2000 rpm
9. Pool methylene chloride extracts
10. Concentrate extract to 1 mL
11. Re-agitate the sample for 5 min in 150 mL toluene
12. Centrifuge for 15 min at 2000 rpm
13. Remove extract
14. Shake manually fly ash for 2 min in 50 mL toluene
15. Centrifuge for 15 min at 2000 rpm
16. Pool toluene extracts
17. Concentrate extract to 1 mL
18. Submit both extracts for liquid scintillation counting

TABLE 5. SOXHLET EXTRACTION RECOVERY OF TCDD-^{14}C STANDARD FROM FLY ASH (8.85 ppb)

Carbon content of sample, %			TCDD-^{14}C recovery, %		
			Solvent extract[a]		
Initial	Added	Total	CH_2Cl_2	Toluene	Total
0	0	0	95	1	96
0	0	0	106	0	106
0	0	0	106[b]	--	106
0	0.1 CB	0.1	85	10	95
0	0.5 CB	0.5	62	30	92
0	5 CB	5	7	76	83
0	5 CB	5	11	66	77
0	5 CB	5	--	85	85
0	10 CB	10	--	85	85
0	5 CAL	5	--	83	83
0	5 AX-21	5	--	86	86
5	0	5	3	95	98
5	0	5	3	94[b]	97
5	0	5	2	86	88
5	0	5	1	85	86
5	0	5	--	92	92
5	5 CB	10	2	87	89
5	5 AX-21	10	--	100	100
5	5 AX-21	10	--	95	95
5	5 AX-21	10	--	96	96

[a]When values are reported for more than one solvent, the sample was extracted sequentially with methylene chloride followed by toluene.

[b]These samples were extracted for 48 h whereas all other samples were extracted for 24 h.

CB - Carbon black, Arthur H. Thomas Company.
CAL - Pittsburgh-activated carbon, Calgon Corporation.
AX-21 - Activated carbon, AX-21, Anderson Development Company.

TABLE 6. SOXHLET EXTRACTION RECOVERY OF OCDD-^{14}C STANDARD FROM FLY ASH (23.0 ppb)

Carbon content of sample, %			OCDD-^{14}C recovery, %		
Initial	Added	Total	Solvent extracts[a]		
			CH_2Cl_2	Toluene	Total
0	0	0	95	3	98
0	0	0	96	3	99
0	0	0	96	3	99
0	0	0	--	99	99
0	0	0	--	99	99
0	0	0	--	98	98
5	0	5	5	95	100
5	0	5	5	94	99
5	0	5	4	96	100
5	0	5	--	106	106
5	0	5	--	97	97
5	0	5	--	96	96
5	5 AX-21	10	0	1	1
5	5 AX-21	10	0	11	11
5	5 AX-21	10	0	4	4
5	5 AX-21	10	0	39	39
5	5 AX-21	10	0	5	5
5	5 AX-21	10	1	49	50
5	5 AX-21	10	--	3	3
5	5 AX-21	10	--	19[b]	19
5	5 AX-21	10	--	49[b]	49
5	5 AX-21	10	--	10	10
5	5 AX-21	10	--	31	31
5	5 AX-21	10	--	6	6
5	5 AX-21	10	--	41	41
5	5 AX-21	10	--	35	35
5	5 AX-21	10	--	44	44
5	5 CAL	10	0	91	91
5	5 CAL	10	--	91	91
Method blank (No fly ash)			--	99[c]	99
Method blank (No fly ash)			--	97[c]	97
Method blank (No fly ash)			--	99[d]	99
Method blank (No fly ash)			--	98[d]	98

[a]When values are reported for more than one solvent, the sample was extracted sequentially with methylene chloride followed by toluene.

[b]These samples were extracted for 48 h whereas all other samples were extracted for 24 h.

[c]Silica gel in extraction thimble was spiked with OCDD-^{14}C.

[d]Extraction thimble was spiked with OCDD-^{14}C.

AX-21 = Activated carbon, AX-21, Anderson Development Company.
CAL = Pittsburgh-activated carbon, Calgon Corporation.

TABLE 7. SUMMARY OF SOXHLET EXTRACTION RECOVERY OF TCDD-^{14}C AND OCDD-^{14}C FROM FLY ASH

Carbon content of sample, %			Recovery efficiency of standard, %[a]			
			TCDD-^{14}C		OCDD-^{14}C	
Initial	Added	Total	CH_2Cl_2	Toluene	CH_2Cl_2	Toluene
0	0	0	100	--[b]	96	99
5	0	5	2	92	5	100
5	5 AX-21	10	--	97	0	24
Method blank	(no fly ash)		--	--	--	98

[a]The values are the averaged recovery efficiencies of spiked ^{14}C-standards after a single 24-h extraction either with methylene chloride or with toluene.

[b]"--" means that samples were not prepared.

handling of expensive glassware that is used in a Soxhlet extraction procedure.

Fly ash containing various levels of carbon were vigorously agitated with methylene chloride and then with toluene. The recovery efficiencies for TCDD-^{14}C from fly ash spiked at 8.85 ppb are given in Table 8. As in the Soxhlet extraction study, the presence of carbon greatly reduces the effective recovery of TCDD-^{14}C with methylene chloride (<10%). A re-extraction of the fly ash samples with toluene gave an additional 60% recovery of TCDD-^{14}C. The total effectiveness of this extraction technique is less than that of the Soxhlet extraction procedure. We did not attempt to optimize this technique or apply it to the extraction of OCDD-^{14}C from spiked fly ash samples. However, one or more options to improve this technique may be to warm or heat the extracting solvent, acidify the fly ash prior to extraction, or sonicate the fly ash in the extracting solvent.

COLUMN CLEANUP CHROMATOGRAPHY METHODS

When dioxins and furans are determined at parts per billion levels (ppb) and lower levels, concentration of the sample extract is required and extensive sample preparation procedures are needed. This is due to the increased ratio of interfering substances to the compounds of interest in the concentrated extract. Many environmental samples, after they undergo an initial extraction or separation such as liquid-liquid or liquid-solid extraction may require one or more column chromatography cleanup procedures. Three optional chromatography columns for the cleanup of extracts from fly ash samples are an acid/base-modified silica gel column, a basic alumina column, and an AX-21 Carbon/Celite 545 column.

The selected column cleanup procedures, as individual columns and as columns in sequence, were evaluated with TCDD-^{14}C and OCDD-^{14}C. The elution sequences that were used for TCDD-^{14}C were based on the ASME's procedures and are outlined in Table 9. However, difficulties were noted and several changes were made when we evaluated the cleanup procedures for OCDD-^{14}C. A 5-mL standard of TCDD-^{14}C (88.5 ng) or OCDD-^{14}C (230 ng) was solvent exchanged into either toluene (n-nonane was used with OCDD-^{14}C) or hexane and was concentrated to 1 mL. The resulting concentrate was applied to the appropriate column. All fractions that were collected for liquid scintillation counting were concentrated to 1 mL and solvent exchanged into n-nonane. Analysis of the solvent exchanged fractions by gas chromatography with flame ionization detection indicated that less then 0.1% of the toluene, if any, remained in the extract after the solvent exchange of toluene with nonane.

The amounts of TCDD-^{14}C recovered in each fraction for the various cleanup steps are summarized in Table 10. Included in the table is a check of labeled residue, if any, remaining in the sample vial after the 1-mL concentrated extract was quantitatively applied to the chromatography column. In evaluation Study A, the TCDD-^{14}C standard was applied to the silica gel column and carried through the basic alumina and AX-21 Carbon/Celite 545 column cleanup procedures. In evaluation Studies D and E, the TCDD-^{14}C standard was applied to the basic alumina column and carried through the AX-21 Carbon/Celite 545 column cleanup procedures. In the remaining evaluation

TABLE 8. AGITATION EXTRACTION RECOVERY OF TCDD-^{14}C STANDARD FROM FLY ASH (8.85 ppb)

Carbon content of sample, %			TCDD-^{14}C recovery, %		
			Solvent extract[a]		
Initial	Added	Total	CH_2Cl_2	Toluene	Total
0	0	0	90	9	99
0	0	0	80	17	97[b]
0	0	0	69	21	90
0	0.1 CB	0.1	22	58	80
0	0.5 CB	0.5	8	66	74
0	5 CB	5	2	60	62
5	0	5	1	48	49
5	0	5	1	52	53[b]
5	0	5	1	67	68
5	5 CB	10	0.5	64	65

[a]When values are reported for more than one solvent, the sample was extracted sequentially with methylene chloride followed by toluene.

[b]These samples were extracted for 10 min whereas all other samples were extracted for 5 min.

CB = Carbon black, Arthur H. Thomas Company.

TABLE 9. COLUMN CLEANUP AND ELUTION SEQUENCE FOR TCDD-^{14}C BASED ON THE ASME's PROCEDURE

SILICA GEL COLUMN:

1. Prewash with 30 mL hexane
2. Apply sample in 1 mL toluene + 5 mL hexane
3. Wash with 5 mL hexane, 2X
4. Elute with 90 mL hexane
5. Concentrate eluate to 1 mL

BASIC ALUMINA COLUMN:

1. Prewash with 5 mL hexane
2. Apply sample in 1 mL hexane
3. Wash with 15 mL hexane
4. Wash with 10 mL 8% methylene chloride in hexane
5. Elute with 15 mL 50% methylene chloride in hexane
6. Concentrate eluate to 1 mL

AX-21 CARBON/CELITE 545 COLUMN:

1. Prewash with 2 mL 50% benzene in ethyl acetate
2. Prewash with 1 mL 50% methylene chloride in cyclohexane
3. Prewash with 2 mL hexane
4. Apply sample in 1 mL hexane
5. Wash with 1 mL hexane
6. Wash with 2 mL 50% methylene chloride in hexane
7. Wash with 2 mL 50% benzene in ethyl acetate
8. Invert column
9. Elute with 4 mL toluene
10. Concentrate eluate to 1 mL

TABLE 10. RECOVERY OF TCDD-^{14}C STANDARD AFTER COLUMN CLEANUP BASED ON THE ASME's PROCEDURE

Column-fraction description	Recovery, %, in Evaluation Study						
	A	B	C	D	E	F	G
SILICA GEL:							
Sample vial	0.6	0.6	0.6				
Sample in 5 mL hexane +10 mL hexane (wash)	71.0	71.0	75.0				
90 mL hexane	*	17.8	15.0				
BASIC ALUMINA:							
Sample vial	0			0.9	0.7	1.4	0.6
Sample in 1 mL hexane +15 mL hexane	0			0	0	0	0
10 mL 8% CH_2Cl_2 in hexane	0			0.3	1.4	0.3	0.4
15 mL 50% CH_2Cl_2 in hexane	*			*	*	86.3	90.5
AX-21 CARBON/CELITE 545:							
Sample vial	0.1			0	0		
Sample in 1 mL hexane +1 mL hexane	0			0	0		
2 mL 50% CH_2Cl_2 in hexane	0			0	0		
2 mL 50% benzene in ethyl acetate	0.7			0	0.5		
4 mL toluene	17.5			86.5	57.3		
4 mL toluene (second portion)					21.7		
TOTAL RECOVERY (Sum of all fractions)	89.9	89.4	90.6	87.7	81.6	88.0	91.5

*This eluate was not analyzed but applied to the next column listed below.

studies, the TCDD-^{14}C standard was submitted to a single column cleanup procedure. Approximately 80% or more of the TCDD-^{14}C was recovered or was accountable. However, areas for possible problems were noted.

Over 70% of the TCDD-^{14}C immediately eluted from the silica gel column in the first 10 mL of hexane. If the analyst is not aware of this, a major portion of the dioxin may be lost. Thus, all effluent from the silica gel column should be collected, pooled, and concentrated to 1 mL. Many of the interferences in the matrix will be removed by the acid/base-modified silica gel column. Strong polar compounds will be absorbed, and the nonpolar materials will be eluted. The data indicate that about 90% of the TCDD-^{14}C was recovered from this cleanup column.

Nonpolar polychlorinated compounds will be absorbed on the basic alumina column; thus, this column is often used as a second step in the cleanup procedure. Also, this column allows for the separation of PCBs from dioxins. Approximately 90% of TCDD-^{14}C was associated with the 15% methylene chloride in hexane fraction. This step must be monitored closely because the activity and uniformity of the alumina may vary with each lot and some of the dioxin may elute in the 8% methylene chloride in hexane fraction.

If additional cleanup is required on a sample extract, the carbon/celite column may be used. Chlorinated dibenzo-p-dioxins are initially adsorbed on this column and the interferences are removed by eluting with solvents of increasing polarity. The PCDDs can then be backwashed from the column by inverting the column and eluting with toluene. The analyst must monitor this procedure carefully. In evaluation Study E (Table 10), approximately 20% of TCDD-^{14}C would be lost if the second 4-mL portion of toluene were not collected.

After evaluating the column cleanup procedures using TCDD-^{14}C, we made a few modifications in the cleanup procedures. The modified column cleanup procedures were evaluated using OCDD-^{14}C. Because the extract of a fly ash sample from the Soxhlet extraction procedure were concentrated to 1 mL of nonane, the OCDD-^{14}C standard in 1 mL of nonane was applied to the silica gel column. The 100 mL of hexane that was used to elute the silica gel column was collected as a single fraction which was concentrated to 1 mL. The concentrated eluent was either applied to the basic alumina column or solvent exchanged in nonane for LSC analysis. Also, we increased the volume of toluene from 4 mL to 10 mL as the last step of the AX-21 Carbon/Celite 545 cleanup procedure. Because the first two fractions collected from this column in our initial evaluation were free of TCDD-^{14}C, the 1 mL of hexane wash was combined with the 2 mL of 50% methylene chloride in hexane wash.

The amounts of OCDD-^{14}C recovered in each fraction for the various cleanup steps are summarized in Table 11. Included in the table is a check of labeled residue, if any, remaining in the sample vial after the 1 mL concentrated extract was quantitatively applied to the chromatography column. The total recovery or accountability of OCDD-^{14}C varied from 40 to 100%. In evaluation Studies E and F, >95% of the spiked OCDD-^{14}C was recovered from the silica gel column.

TABLE 11. RECOVERY OF OCDD-^{14}C STANDARD AFTER COLUMN CLEANUP BASED ON MODIFICATION OF THE ASME'S PROCEDURE

Column-fraction description	Recovery, %, in Evaluation Study													
	A	B	C	D	E	F	G	H	I	J	K	L	M	N
SILICA GEL:														
Sample vial	0	0	0.1	0.2	**	**								
Sample in 1 mL nonane	*	*	80.7	74.1	96.0	98.8								
+100 mL hexane														
BASIC ALUMINA:														
Sample vial	0	0					0.7	0	**	**				
Sample in 1 mL hexane	0.9	0					0	0	**	**				
+15 mL hexane														
10 mL 8% CH_2Cl_2 in hexane	24.8	29.2					7.1	7.2	**	**				
15 mL 50% CH_2Cl_2 in hexane	*	*					92.2	92.7	85.2	86.1				
AX-21 CARBON/CELITE 545:														
Sample vial	0	0												
Sample in 1 mL hexane	0	0									0.2	0.1	**	**
+1 mL hexane+2 mL 50% CH_2Cl_2 in hexane											1.3	0	**	**
2 mL 50% benzene in ethyl acetate	0	0									1.6	3.7	**	**
10 mL toluene	49.2	56.8									57.0	39.8	79.7	83.6
TOTAL RECOVERY (Sum of all fractions)	74.9	86.0	80.8	74.3	96.0	98.8	100.0	99.9	85.2	86.1	60.1	43.6	79.7	83.6

*This eluate was not analyzed but applied to the next column listed below.
**This eluate was collected but not analyzed.

The cleanup procedures for OCDD-^{14}C with the basic alumina column were identical with those used for TCDD-^{14}C. Although a small amount, if any, of OCDD-^{14}C remained on the column, the elution with 10 mL of 8% methylene chloride in hexane did contain various amounts of the OCDD-^{14}C. If this fraction were discarded, >20% of OCDD-^{14}C may be lost.

The cleanup procedures for OCDD-^{14}C with the AX-21 Carbon/Celite 545 retained various amounts of the spiked standard. In evaluation Studies M and N, 80% of the spiked OCDD-^{14}C was recovered.

Although we made a few changes in the ASME's cleanup procedures, the evaluation of these changes with OCDD-^{14}C revealed additional areas for possible problems. A major concern is the possible loss of dioxins, especially those that are highly chlorinated, during the basic alumina column cleanup procedure.

In an attempt to reduce the amount of OCDD-^{14}C eluted from the basic alumina column with 10 mL of 8% methylene chloride in hexane, we changed to 10 mL of 5% of methylene chloride in hexane. The evaluation of this proposed elution sequence is reported in Table 12. About 3% of OCDD-^{14}C eluted with the 5% methylene chloride in hexane fraction. This is a problem that may not be easily resolved. Certainly this fraction must be analyzed for the presence of trace amounts of dioxins, especially those that are highly chlorinated and when recovery of surrogate standards are low. The results obtained in evaluation Study A (Table 12) demonstrate another problem that must be addressed. The technical skills and experience of the analyst may bias the data. Evaluation Study A was performed by a professional member of our laboratory staff with limited experience with the protocol. We recommend that the procedures in this report be implemented by or under the close supervision of analysts with experience in trace analyses.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Although the use of radiolabeled dioxins and LSC is a sensitive and simple method to evaluate each step of the analytical method for the recovery of dioxin in fly ash, it does lack specificity. Should the dioxin-^{14}C undergo any chemical changes during the sample extraction and subsequent column cleanup procedures, LSC will only identify the ^{14}C label and not the chemical structure of the compound carrying the label. Therefore, confirmation by a second analytical method was needed to validate the data in this report. In this study, the presence of TCDD was confirmed by GC/MS. Replicate fly ash samples were carried through the Soxhlet extraction procedures. After the extracts were concentrated to 1 mL, some of the samples were submitted for LSC while others were submitted for GC/MS analysis. LSC indicated that approximately 93% of the labeled material was recovered. The recovery of 2,3,7,8-TCDD, as determined by GC/MS, was 91%.

In another study, a fly ash sample was submitted to the Soxhlet extraction procedures and then the concentrated extract was put through all three column cleanup procedures. The final eluate was concentrated to 1 mL and split. Half of the eluate was analyzed by LSC and the other half by GC/MS. LSC showed a 77% recovery of TCDD-^{14}C, and GC/MS showed a 67% recovery of TCDD. However, LSC of five additional samples gave a recovery range of 60% to 113%. If the LSC results of all the elution fractions from the cleanup proce-

TABLE 12. RECOVERY OF OCDD-^{14}C STANDARD AFTER COLUMN CLEANUP BASED ON A PROPOSED ELUTION SEQUENCE.

Column-Fraction description	Recovery, %, in Evaluation Study[a]			
	A	B	C	D
SILICA GEL:				
Sample vial	0.2	0.1		
Sample in 1 mL nonane +100 mL hexane	*	*		
BASIC ALUMINA:				
Sample vial	0.1	0.1	0	0
Sample in 1 mL hexane +10 mL hexane	0	0	0	0.2
10 mL 5% CH_2Cl_2 in hexane	0	0	2.7	3.4
15 mL 50% CH_2Cl_2 in hexane	*	*	95.7	94.9
AX-21 CARBON/CELITE 545:				
Sample vial	0.4	0.2		
Sample in 1 mL hexane +1 mL hexane+2 mL 50% CH_2Cl_2 in hexane	0	0		
2 mL 50% benzene in ethyl acetate	0	0		
10 mL toluene	12.0	79.3		
TOTAL RECOVERY (Sum of all fractions)	12.7	79.7	98.4	98.5

*This eluate was not analyzed but applied to the next column listed below.

[a]Evaluation Study A was conducted by an experienced analyst with limited experience with this protocol.

dures are included, then the total recovery of TCDD-^{14}C was in a range of 80% to 117%. These differences demonstrate why it is extremely important to analyze all elution fractions when the recovery of dioxin surrogate standards or spiked standards is low.

SPECIAL CONSIDERATIONS

If trace compounds in complex environmental samples are to be accurately determined, appropriate analytical procedures must be selected and carefully followed by the analyst. The extraction and cleanup procedures used in the analyses of fly ash for the determination of PCDD and PCDF must be validated by the laboratory and the individual analyst performing the analysis. Laboratory control samples (spiked matrix samples) must be carried through the entire analytical method, which includes sample preparations, cleanup of sample extracts, and instrumental analysis. Procedural details and analytical techniques, such as the cycling of solvent in the Soxhlet extractor, the concentration of the analyte in the sample extract, the transfer of solutions, the exchange of solvents, the packing of the chromatographic media into columns, and the volume and composition of extracting solvents, are extremely important. Variable loss of dioxins can occur in each of these steps. All extracts, eluate fractions, and residues generated during an analysis need to be saved for additional analysis when the recovery of spiked standards or surrogate standards are extremely low in the initial analysis. If there is a question about low recovery after the final eluate is analyzed, the other eluates may have to be analyzed.

As TCDD-^{14}C and OCDD-^{14}C were monitored through each step of this analytical method, several areas were noted that may affect the recovery of dioxins from fly ash. A layer of silica in the bottom of the glass extraction thimble will prevent the fly ash from clogging the pores or the fine particles from passing into the boiling flask. The extracting solvent did not readily drain through the very fine particles of fly ash. If extraction thimbles other than glass are used, the solvent may preferentially drain through the sides extended above the sample and not through the sample. To allow more time for the solvent to drain through the sample at the completion of a cycle, the extraction thimble was raised about 1 cm above the bottom of the extraction chamber.

Preliminary data indicate that the recovery may be improved if, after the Soxhlet extraction procedure, the toluene is exchanged with n-nonane. Thus, when the concentrated extract is applied to the head of the acid/base-modified silica gel column, the dioxin will be in an aliphatic solvent that is less polar.

During the cleanup procedures, occasionally a small amount of TCDD-^{14}C or OCDD-^{14}C would elute in an unexpected fraction. Specifically, in the acid/base-modified silica column, TCDD-^{14}C came through immediately with hexane. In later studies, hexane was collected as one fraction from the silica gel column. In the basic alumina column, a small amount of OCDD-^{14}C eluted in the second fraction containing 8% methylene chloride in hexane. On two occasions, OCDD-^{14}C in this fraction exceeded 10% of the spiked quantity. We recommend that 3% or 5% methylene chloride in hexane be used in this step to reduce the potential for loss of dioxin. However, additional studies with other fly ash samples must be conducted to confirm this recommendation.

In the last incident, we discovered that TCDD-^{14}C and OCDD-^{14}C may remain on the AX-21 Carbon/Celite 545 column after the recommended elution with 4-mL toluene. In our later studies, we routinely used 10 mL of toluene for this final step.

Careful attention to column preparation is a must in this analysis. The condition and amounts of chromatography media must be monitored and documented. In later studies, all three types of columns were prepared as wet columns. This prevented air entrapment and channeling of eluents. Also, the volume, composition of, and sequence of eluents must be identical for each cleanup procedure.

With every set of samples that are analyzed, laboratory control samples, surrogate spiking standards, replicate analyses, and method blanks must be included. The extraction and cleanup procedures to determine dioxins in fly ash samples must be implemented by or under close supervision of analysts with experience in trace analyses.

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APPENDIX A

PROPOSED MODIFICATIONS TO THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS, U.S. DEPARTMENT OF ENERGY, AND U.S. ENVIRONMENTAL PROTECTION AGENCY "ANALYTICAL PROCEDURES TO ASSAY STOCK EFFLUENT SAMPLES AND RESIDUAL COMBUSTION PRODUCTS FOR POLYCHLORINATED DIBENZO-P-DIOXINS (PCDD) AND POLYCHLORINATED DIBENZOFURANS (PCDF)."

To establish base line data for the efficiency of dioxin recover from fly ash samples, we followed ASME's draft method, September 18, 1984, entitled "Analytical Procedures to Assay Stock Effluent Samples and Residual Combustion Products For Polychlorinated Dibenzo-p-dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF)." As our experimental data were generated, potential problem areas were observed. Those changes which resulted in improvements were incorporated in the remaining phases of this work assignment to circumvent those problems unique to our experimental study and to permit the continuation of data generation. Those changes that were made were evaluated with fly ash samples spiked with tetra- and octa-CDD. Thus, the data presented in this report represent an evolution from the original ASME's method to the final modifications used by us.

The ASME's method is an appropriate procedure for the determination of dioxins and dibenzofurans in fly ash. However, when unique situations occur either because of the low levels of dioxin in fly ash samples or the amount of carbon content of the fly ash samples and the amount of dioxin determined is extremely low or not detected, the proposed changes to the ASME's method may be desirable.

2. Reagents and Chemicals

2.2 The aliphatic solvent n-nonane should be included in the list of organic solvents. After extracting with toluene in a Soxhlet extractor, the toluene was solvent exchanged with n-nonane.

2.5 The silica gel was conditioned (activated) by heating at 130 °C for 6 hours prior to use.

2.8 Activated carbon, AX-21 grade, Super A, from Anderson Development Company was used to prepare the Carbon/Celite chromatography column.

6.3 Solid Sample

The analyst must confirm that the Soxhlet apparatus is functioning correctly. The thimble may have to be raised in the Soxhlet apparatus to allow draining of the extracting solvent. The extracting solvent must follow downward through the fly ash sample. Approximately 1 g of anhydrous sodium sulfate was placed in the bottom of the extraction thimble followed by a 10-g sample of fly ash.

7. Procedures for Cleanup and Fractionation of Sample Extracts

The Soxhlet extract is concentrated to a volume of 1 mL on a hot plate with a stream of dry nitrogen and solvent exchanged with n-nonane. The concentrated nonane extract is transferred quantitatively to the combination silica gel column.

7.1 Combination Silica Gel Column:

The sample extract in 1 mL of nonane is added to the column along with two 5-mL rinses of hexane. The column is eluted with an additional 10 mL of hexane. The entire elute collected is concentrated to a volume of 1 mL.

7.2 Basic Alumina Column:

Transfer the concentrated extract from the combination silica gel column to the top of the basic alumina column and elute the column sequentially with 10 mL hexane, 10 mL of 5% methylene Chloride, in hexane, and 15 mL of 50% methylene chloride in hexane. Save the first two elute fractions for analysis if dioxin recovery is low.

7.3 PX-21 Carbon/Celite 545 Column:

AX-21 carbon was used in the preparation of this column.

Load the extract (in 1 mL of hexane) from the alumina column onto the top of the column, along with 1 mL hexane rinse. Elute the column with 2 mL of 50% methylene chloride in hexane and 2 mL of 50% benzene in ethyl acelute. Save these elutes for analysis if the recovery of dioxin is low. Insert the column and reverse elute ? with 10 mL of toluene, retaining this final elute for analysis.